



## PATENT SPECIFICATION

NO DRAWINGS

935.595

Date of Application and filing Complete Specification: March 15, 1961.

No. 9552/61.

Application made in Switzerland (No. 2927) on March 15, 1960.

Complete Specification Published: Aug. 28, 1963.

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Index at acceptance:—Class 2(4), PQ2C, PQ2K (3:4A:5), PQ2L(1:3), PQ2N1A.

International Classification:—C09b.

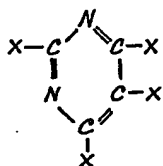
## COMPLETE SPECIFICATION

## New Anthraquinone Vat Dyestuffs and their manufacture and use

We, CIBA LIMITED, a body corporate organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

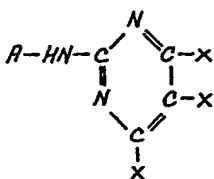
This invention provides valuable new water-insoluble anthraquinone vat dyestuffs corresponding to the general formula

(1)



in which one X represents the residue of a monoaminoanthraquinone which may contain fused on carbocyclic or heterocyclic rings and which is free from sulphonic and carboxylic acid groups and which is bound through the —NH-bridge to the pyrimidine ring, two X's represent amino, alkylamino, hydroxyalkylamino, alkoxyalkylamino, cycloalkylamino or phenylamino groups and the fourth X represents a hydrogen atom or an alkyl, nitro, amino, alkylamino, hydroxyalkylamino, alkoxyalkylamino, cycloalkylamino or phenylamino group.

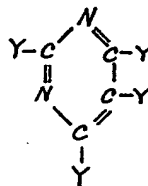
Of special interest are dyestuffs which correspond to the general formula



[Price 4s. 6d.]

in which A represents the residue of a monoaminoanthraquinone which may contain fused on carbocyclic or heterocyclic rings, two X's represent amino, alkylamino, hydroxyalkylamino, cycloalkylamino or phenylamino groups and the third X represents a hydrogen atom or an alkyl, nitro, amino, alkylamino, hydroxyalkylamino, cycloalkylamino or phenylamino group.

The new dyestuffs may be obtained by a process, wherein a monoaminoanthraquinone which may contain fused on carbocyclic or heterocyclic rings and which is free from sulphonic and carboxylic acid groups is condensed with one mol of a pyrimidine derivatives of the general formula



in which at least three Y's represent halogen atoms, and the fourth Y may be a hydrogen or halogen atom, a nitro or alkyl group, and every mobile halogen atom remaining in the resulting primary condensation product is exchanged for an amino, alkylamino, hydroxyalkylamino, alkoxyalkylamino, cycloalkylamino or phenylamino group.

As monoaminoanthraquinones there may be mentioned, for example, 1-aminoanthraquinone and simple substitution products thereof, such, for example, as 1-amino-4-, -5- or -6-methoxy-anthraquinone, 1-amino-3-, -6- or -7-chloranthraquinone, 1-amino-4-, -5- or 8-acylamino- and more especially -benzoylamino- anthraquinones. The latter may be substituted in the benzoyl residue, for example, by halogen atoms or methoxy, alkyl, trifluoromethyl, sulphonamide or alkylsulphone groups.

There may also be mentioned aminoanthraquinones that further contain fused-on carbocyclic or heterocyclic rings, for example

- 4 - aminoanthraquinone - 2:1(N) - acridone,
- 5 - amino - 1:9 - isothiazole - anthrone,
- 4- or 5 - aminoanthrapyrimidine,
- mono - aminoacedianthrones,
- 4- or 5 - amino - 1:1<sup>1</sup> - dianthrimide - carbazole,
- 4- or 5 - amino - 5<sup>1</sup> - benzoylamino - dianthrimide - carbazole or
- 4 - amino - 4<sup>1</sup> - benzoylamino - dianthrimide - carbazole,
- 4 - amino - anthrapyridones,
- aminodibenzanthrone, aminoisodibenzanthrone, aminodibenzpyrenequinone, aminoanthranthrone, aminobenzanthrone and aminoflavanthrone.

As pyrimide derivatives of the formula (2) there may be mentioned:

- 2:4:6 - trichloropyrimidine,
- 2:4:6 - tribromopyrimidine,
- 2:4:5:6 - tetrachloropyrimidine, and
- 2:4:6 - trichloro - 5 - nitropyrimidine,

Every mobile halogen atom that remains in the resulting primary condensation product is exchanged for an amino group which may be substituted, for example, by reaction with ammonia or a phenylamine, such as aniline, ortho-, meta, or para-toluidine, or preferably with an aliphatic amine such, for example, as methylamine, dimethylamine, ethylamine, diethylamine, isopropylamine or butylamine, and more especially a hydroxyalkylamine, such as  $\beta$ -hydroxyethylamine, di-(hydroxyethyl)-amine,  $\gamma$ -hydroxypropylamine or an alkoxyalkylamine such as  $\beta$ -methoxyethylamine, or a cycloalkylamine such as cyclohexylamine.

The reactions are advantageously carried out in an inert organic solvent, for example, nitrobenzene, chlorobenzene, ortho-dichlorobenzene or dimethylformamide, at an elevated temperature. In general, it is not necessary to isolate the halogenated primary condensation product, and it is of advantage to carry out both reactions in the same vessel.

The dyestuffs of the invention can be used, for example, as pigments, for colouring a wide variety of materials, and more especially for dyeing or printing textile materials of natural or regenerated cellulose by the conventional vat dyeing or printing methods.

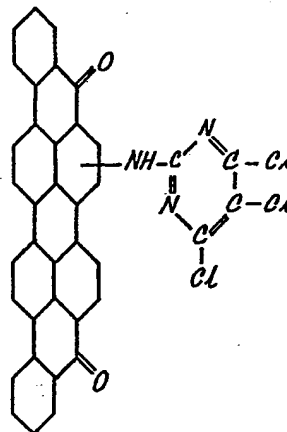
The following Examples illustrate the invention, the parts and percentages being by weight unless otherwise stated, and the relationship of parts by weight to parts by volume being the same as that of the kilogram to the litre:

#### EXAMPLE 1.

9.4 Parts of aminodibenzanthrone are suspended, while stirring, in 200 parts of dry nitrobenzene and the whole is heated to 160 to 170°C. A solution of 6 parts of 2:4:5:6-tetrachloropyrimidine in 50 parts of nitrobenzene is then added, followed by the addi-

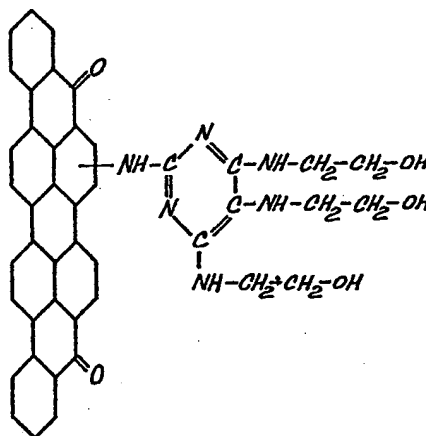
tion of 0.5 part of pyridine, whereupon the mixture is stirred on for 20 hours at 170°C and then cooled to room temperature. The resulting condensation product of the probable formula

70



is then filtered off and washed successively with nitrobenzene and acetone. The filter cake is stirred in small portions at 150 to 160°C into 100 parts of monoethanolamine and the mixture is refluxed for 2 hours, allowed to cool, poured into water and the dyestuff of the probable formula

75



is filtered off, washed successively with water and acetone, and dried *in vacuo* at 60 to 70°C.

80

When dry, the new dyestuff forms a black powder which dyes cotton and regenerated cellulose from an alkaline hydrosulphite vat valuable black shades having excellent properties of fastness.

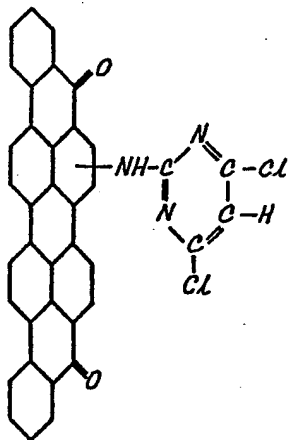
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#### EXAMPLE 2.

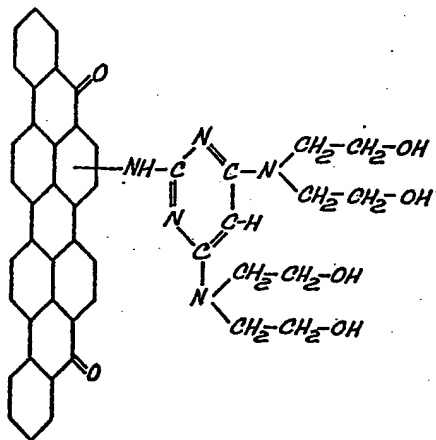
9.4 parts of aminobenzanthrone are suspended with stirring in 200 parts of dry nitrobenzene and the whole is heated to 160 to

90

- 170°C. A solution of 5.5 parts of 2:4:6-trichloropyrimidine in 40 parts of nitrobenzene is then added, the mixture is treated with 0.5 part of pyridine, stirred on for 20 hours at 190°C and then cooled to room temperature. The resulting condensation product of the probable formula



- is filtered off and washed with nitrobenzene and then with acetone. The filter cake is cautiously stirred in small portions at 160 to 170°C into 100 parts of diethanolamine and the mixture is stirred on for 2 hours at 170 to 180°C. The reaction mixture is then poured over 1000 parts of ice, and the dyestuff of the probable formula

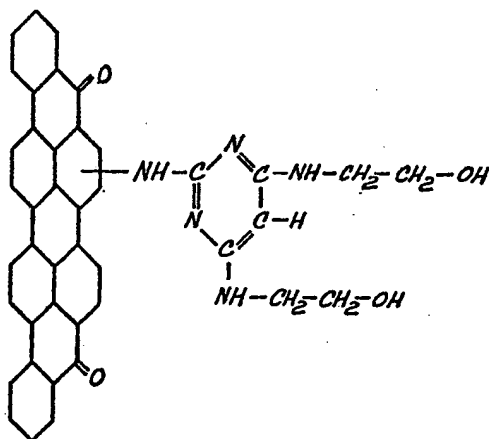


- is filtered off, washed with water and then with acetone, and dried *in vacuo* at 60 to 70°C. The new dyestuff dyes cotton and regenerated cellulose from a blue-violet vat black shades having excellent fastness properties.

#### EXAMPLE 3.

- The condensation product from aminodibenzanthrone and 2:4:6-trichloropyrimidine

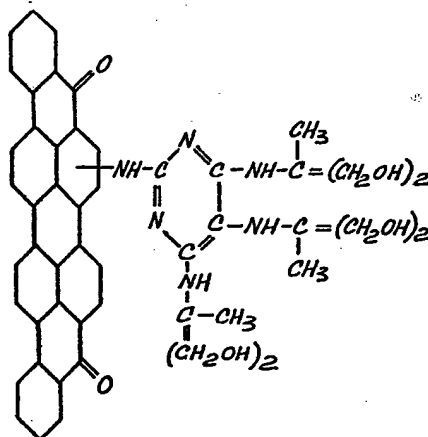
described in the first paragraph of Example 2 is cautiously stirred into 100 parts of boiling ethanolamine and the mixture is refluxed for 1½ hours. The dyestuff of the probable formula



is isolated as described in Example 2. It dyes cotton and regenerated cellulose black shades of excellent fastness properties.

#### EXAMPLE 4.

- 5.0 parts of the condensation product from aminodibenzanthrone and 2:4:5:6-tetrachloropyrimidine prepared as described in Example 1 are heated in 80 parts of dimethylformamide and 20 parts of 2-amino-2-methyl-1:3-propanediol for 10 hours at 190°C in an autoclave equipped with a stirrer; the mixture is then poured into water and the dyestuff is filtered off and dried. This new dyestuff of the probable formula

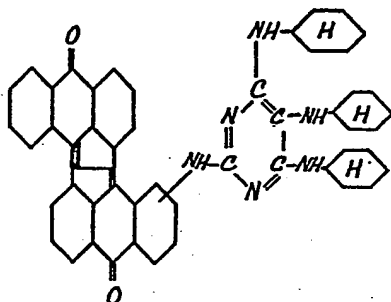


dyes cotton and regenerated cellulose from a blue-violet hydrosulphite vat black shades having very good fastness properties.

Dyestuffs that have equally good properties are obtained by replacing in this Example 2-amino-2-methyl-1:3-propanediol by an equal amount of 2-aminobutanol or 2-amino-2-methylpropanol or tri-(hydroxymethyl)-amino-methane.

#### EXAMPLE 5.

A mixture of 15 parts of aminoacedianthrone, 250 parts of nitrobenzene, 15 parts of 2:4:5:6-tetrachloropyrimidine and 1 part of pyridine is heated with stirring for 9 hours at 170 to 175°C and then allowed to cool. The condensation product is filtered off, washed with nitrobenzene and thoroughly expressed. The filter cake is stirred into 150 parts of cyclohexylamine and the mixture is refluxed for 2 hours and allowed to cool. The excess amine is then expelled with steam and the dyestuff is filtered off and dried. This dyestuff of the probable formula



dyes cotton and regenerated cellulose from an alkaline hydrosulphite vat very fast brown shades.

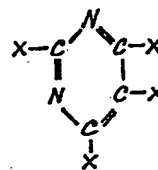
When in this Example cyclohexylamine is replaced by an equal amount of aniline and the mixture is heated for 2 hours at 180°C, a dyestuff of similar properties is obtained.

#### EXAMPLE 6.

0.8 Part of the dyestuff obtained as described in Example 1 in 100 parts of water is vatted in the presence of 6 parts by volume of sodium hydroxide solution of 30% strength with 2.4 parts of sodium hydrosulphite at 50 to 60°C. The stock vat thus prepared is added to a solution of 6 parts by volume of sodium hydroxide solution of 30% strength and 0.8 part of sodium hydrosulphite in 300 parts of water. 10 Parts of cotton satin are dyed in the resulting dyebath for 1 hour at 60 to 80°C with the addition of 12 parts of sodium chloride. The cotton is then squeezed, oxidised in air, rinsed, acidified, again rinsed and soaped at the boil. A strong black dyeing is obtained which has very good properties of fastness.

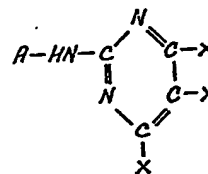
#### WHAT WE CLAIM IS:—

1. Water-insoluble vat dyestuffs of the general formula



in which one X represents the residue of a monoaminoanthraquinone which may contain fused on carbocyclic or heterocyclic rings and which is free from sulphonic acid and carboxylic acid groups and which is bound through the —NH—bridge to the pyrimidine ring, two X's represent amino, alkylamino, hydroxyalkylamino, alkoxyalkylamino, cycloalkylamino or phenylamino groups and the fourth X represents a hydrogen atom, an alkyl, nitro, amino, alkylamino, hydroxyalkylamino, alkoxyalkylamino, cycloalkylamino or phenylamino group.

2. Vat dyestuffs as claimed in claim 1, which correspond to the general formula



in which A represents the residue of a monoaminoanthraquinone which may contain fused on carbocyclic or heterocyclic rings, two X's represent amino, alkylamino, hydroxyalkylamino, cycloalkylamino or phenylamino groups and the third X represents a hydrogen atom, an alkyl, nitro, amino, alkylamino, hydroxyalkylamino, cycloalkylamino or phenylamino group.

3. Vat dyestuffs as claimed in claim 1 or 2, in which at least one X or the residue A—NH— represents the residue of 4-aminoanthraquinone-2:1(N)-acridone, 5-aminoanthrapyrimidine, a monoaminoacedianthrone, 4- or 5-amino-1:1'-dianthrime-carbazole, 4- or 5-amino-5'-benzoylamino-dianthrime-carbazole, 4-amino-4'-benzoylamino-dianthrime-carbazole, 4-amino-anthrapyridone, an amino-dibenzanthrone, an aminoisodibenzanthrone, an aminodibenzpyrenequinone, an amino-anthranthrone an aminobenzanthrone or an aminoflavanthrone.

4. Vat dyestuffs as claimed in claim 2, in which A represents a dibenzanthrone residue, two X's represent hydroxyalkylamino groups and the third X represents a hydrogen atom

- or a hydroxylalkylamino group.
5. Any one of the vat dyestuffs obtainable as end products of Examples 1—5 herein.
6. A process for dyeing or printing textile materials of cellulose, wherein a dyestuff claimed in any one of claims 1 to 5 is used.
7. A dyeing process conducted substantially as described in Example 6 herein.
8. Cellulose textile materials which have been dyed or printed by the process claimed in claim 6 or 7.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press  
(Leamington) Ltd.—1963. Published by The Patent Office, 25 Southampton Buildings,  
London, W.C.2, from which copies may be obtained.